NASA TT F-8207

NITROGEN DISSOCIATION IN THE UPPER ATMOSPHERE

by A. D. Danilov

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON April 1962

DRAFT TRANSLATION NASA TT F-8207

APR 9 1962

NITROGEN DISSOCIATION IN THE UPPER ATMOSPHERE

(K voprosu o dissotsiatsii azota v verkhney atmosfere)

Geomagnetizm i Aeronomiya
Tom I, No. 2,
pp. 174-177,
Izd-vo A. N.SSSR, 1961

by A. D. Danilov

ABSTRACT

Possible ways of atomic nitrogen formation in the upper atmosphere are examined. It is shown, that photochemical reactions lead to a high rate of nitrogen formation at 200 to 300 km altitudes. On the basis of experimental data an estimate is made of the number of nitrogen atoms in the atmosphere column above 200 km. The distribution of N concentration with altitude is obtained.

author

COVER-TO-COVER TRANSLATION

The question of chemical composition of the atmosphere at altitudes beyond 150 — 200 km, and of nitrogen dissociation in particular, constitutes one of the most important problems of upper atmosphere physics.

Inasmuch as the dissociation coefficient of the nitrogen molecule by direct effect of solar radiation

$$N_2 + h\nu \rightarrow N + N$$

is very small, and constitutes about 10^{-12} sec^{-1} [1], the N_2 dissociation cannot play a substantial part in the upper atmosphere. Nicolet pointed to the dissociative recombination reaction of the

ions N_2^+ (see ref. [2]):

$$N_2^+ + e \rightarrow N + N \qquad (1)$$

as a possible source of atomic nitrogen at great altitudes. However, the absence to-date of data on ion concentration in the atmosphere and on the coefficient of the reaction (1) rate did not allow a quantitative investigation of this question.

The results of the study of the ionic composition of the atmosphere in the 100 – 500 km altitude range carried out by V. G. Istomin [3, 4, 5] with the aid of geophysical rockets and in the third Soviet artificial satellite of the Earth, have shown that NO^+ and N_2^+ ions exist at these heights in substantial quantities. By their combination with electrons according to the reactions (1) and (2), they lead to nitrogen atoms' formation :

$$NO^+ + e \rightarrow N + O \qquad (2)$$

The coefficient of the dissociative recombination rate (1, 2), lately has been measured experimentally several times [6, 7], leading to the value 10^{-6} cm^3 sec^{-1}. Besides, the reactions

$$O^+ + N_2 \rightarrow NO^+ + N, \qquad (3)$$

$$N^+ + N_2 \rightarrow N_2^+ + N, \qquad (4)$$

examined in references [8, 9] as the source of ion NO^+ and N_2^+ formation, also lead to the formation of neutral nitrogen atoms. Therefore, the total rate of atomic nitrogen formation at the given altitude in cm^3 per second is equal to the sum of reaction rates (1)through(4):

$$V_N^{form.} = V_1 + V_2 + V_3 + V_4.$$

Inasmuch as according to [8, 9]

$$V_4 = V_1 \text{ and } V_3 = V_2,$$

$$(V_N^{form} = 2V_1 + 2V_2 = 2\alpha n_e \{[NO^+] + [N_2^+]\}, \qquad (5)$$

where α is the coefficient of the dissociative recombination reaction rate. The computed magnitudes V_N^{form} are tabulated hereafter

H, км	$[NO^+]$	$[N_2^+]$	n_e	V_N^{form}
160	$1{,}4\cdot10^5$	$<10^3$	$1{,}8\cdot10^5$	$3{,}2\cdot10^4$
200	$1{,}9\cdot10^5$	$4{,}8\cdot10^3$	$4{,}0\cdot10^5$	$1{,}2\cdot10^5$
300	$5{,}8\cdot10^4$	$1{,}1\cdot10^4$	$2{,}0\cdot10^5$	$3{,}1\cdot10^5$
400	$1{,}1\cdot10^4$	$2{,}1\cdot10^3$	$1{,}4\cdot10^5$	$5{,}1\cdot10^4$
500	$1{,}2\cdot10^3$	$1{,}0\cdot10^3$	$1{,}0\cdot10^5$	$1{,}0\cdot10^4$

The magnitude n_e is taken according to the experimental data of reference [10]. It may be seen from the above table that the rate of atomic nitrogen formation as a result of ion-exchange reactions is rather high. It is necessary to stress that the obtained high values V_N do not depend essentially on the proposed mechanisms of ion NO^+ and N_2^+ formation, but are only based upon the observed concentrations of these ions, and the experimentally obtained coefficient of the dissociative recombination rate.

There arises a natural question about the mechanism of nitrogen atom vanishing, which under the equilibrium conditions should compensate the N formation:

$$V_N^{form.} = V_N^{vanish.},$$

Nicolet [2, 11] expressed more than once the idea that the vanishing of nitrogen atoms takes place in the atmosphere along the system of reactions:

$$\left.\begin{array}{l} 1.\ N + O_2 \rightarrow NO + O \\ 2.\ NO + N \rightarrow N_2 + O \end{array}\right\} \qquad (6)$$

Besides, for the explanation of atomic nitrogen recombination, the following reactions were proposed by various authors:

$$N + N \rightarrow N_2 + h\nu, \qquad (7)$$

$$N + N + M \rightarrow N_2 + M' \qquad (8)$$

$$\left.\begin{array}{l} 1.\ N+O+M \rightarrow NO+M' \\ 2.\ NO+N \rightarrow N_2+O \end{array}\right\} \qquad (9)$$

However, the system of reactions (6) can hardly play any somewhat significant role in the atmosphere above 200 km, inasmuch as according to contemporary concepts, molecular oxygen is strongly dissociated as of 150 — 160 km altitudes. The reactions (8) and (9) cannot be sufficiently effective at great altitudes either, for even Mitra [12] has already shown, that the triple collision reactions are only significant to 80 — 90 km altitudes, their effectiveness dropping sharply above that range. As to the reactions (6_2) and (9_2), their reaction rate is rather high, and constitutes 10^{-13} cm^3 sec^{-1}. However, according to experimental data [13], the atmosphere lacks somewhat significant balanced NO concentrations, while the corresponding reactions (6_1) and (9_1) are ineffective.

Therefore, the only apparently real way of atom N vanishing is the recombination reaction with emission (7).

In order to obtain a concentration of atomic nitrogen at the examined altitudes, while lacking reliable data on the reaction rate coefficient, let us proceed in the following manner: Let us postulate that atomic nitrogen constitutes one half of the total density at 500 km altitude, which corresponds to $[N]_{500} = 1.8 \cdot 10^7 cm^{-3}$. Then, considering from the equilibrium condition, that reaction (7) is responsible for N vanishing, we obtain:

$$V_N^{form} = V_N^{van.} = [N]^2 \alpha_7, \qquad (10)$$

where α_7 is the coefficient of reaction (7) rate. Knowing $[N]$ and $V_N^{form.}$ we may find from (10) for 500 km:

$$\alpha_7 = \frac{1.0 \cdot 10^4}{(1.8 \cdot 10^7)^2} = 3.0 \cdot 10^{-11} см^3 сек^{-1}$$

Considering the magnitude α_7 as constant for all altitudes, one may find from (10) the value $[N]$ for all the examined altitudes

according to the value of V_N brought out in the Table:

H, км	200	300	400	500
[N], $см^{-3}$	$6{,}0\cdot10^7$	$1{,}0\cdot10^8$	$4{,}1\cdot10^7$	$1{,}8\cdot10^7$

The obtained concentrations of atomic nitrogen cannot be substantially changed, at least in the sense of increase, despite their being based upon an arbitrary choice of the magnitude $[N]_{500}$. If indeed we take, say at 400 km altitude a concentration N twice as great as that brought out, the coefficient α_7 will decrease 4 times, while the concentration of N increases twofold at all altitudes, and the atomic nitrogen will thus become the only component of the atmosphere at 500 km altitude. Greater increases of [N] at lower altitudes will lead to still sharper contradictions between [N] and the total density in the 400 — 500 km altitude range.

On the other hand, the only way of checking the validity of the obtained quantity of N in the atmosphere column consists in the following reasoning: There is in the spectra of solar ultraviolet radiation, obtained at 200 km during rocket launchings [14] a reliably identified atomic nitrogen line 1200 Å, corresponding to nitrogen atom's $^4S^\circ$ transition to the basic level. Knowing this line's intensity, obtained in the spectrogram, relative to that of the L_α line, which does not undergo notable absorption at these altitudes, and having taken the value of 3 erg/cm sec for the line's L_α intensity, we obtain for the value of line L_α intensity at 200 km altitude, the magnitude 0.03 erg/cm sec. The estimate of that line's intensity beyond the limits of the terrestrial atmosphere, made on the basis of the work [15], give the magnitude of 0.015 to 0.020 erg/cm sec. The comparison of both intensities, having a 2 — 3 times precision, shows that the line 1200 Å is absorbed in the atmosphere to 200 km altitude no more than 2 times.

Starting from the formula of emission line absorption [16]

$$I_H = I_\infty e^{-\alpha\sqrt{N}},$$

where

$$\alpha = \frac{4e^2\lambda_0\sqrt{f}\sqrt{\frac{\pi}{6}}}{m_e c^2 \Delta\lambda_D},$$

it is easy to obtain the estimate of the upper limit of atom N quantity in the atmosphere column above 200 km. Calculations give for the 1200 Å line :

$$N_N^{200} \leqslant 2 \cdot 10^{15} at/cm^2.$$

If we add the magnitudes [N] brought out in the given work, we obtain the following quantity of atoms in the column for 200 km :

$$N_N^{200} \leqslant 2{,}2 \cdot 10^{15} at./cm^2,$$

which does not contradict the previous magnitude within the limits of precision.

The obtained results may be interpreted as follows : the nitrogen dissociation at altitudes below 400 km is small — the atomic nitrogen becomes the essential atmosphere component only at 500 km altitude and above. The course with altitude of atomic nitrogen concentration is about constant, and the obtained concentrations of N apparently constitute the upper limit of possible values [N].

The mechanism of atomic nitrogen recombination proposed by Nicolet, cannot assure a sufficient rate of nitrogen atom vanishing at 300 to 400 km altitudes, where these atoms' rate of formation is maximum, since there is practically no molecular oxygen at these altitudes. Reaction (7) is capable of providing the necessary rate of N vanishing at all altitudes and for a high coefficient of the rate α_7, of the order of 10^{-11} cm^3 sec^{-1}. It is possible that there are other, still unknown mechanism of atomic nitrogen recombination in the atmosphere, capable of equilibrating the high rate of N formation.

The fact that there are in the night sky glow atomic nitrogen lines is not in contradiction with the obtained low N concentrations in the 200 — 400 km altitude range, inasmuch as this glow, as shown in [17], is well explained by the reaction of ion N_2^+ dissociative recombination. Similarly, the presence in the atmosphere of N^+ ions may be explained by the dissociative ionization of molecules N_2 [18] :

$$N_2 + h\nu \longrightarrow N^+ + N + e$$

without resorting to significant concentrations of atomic nitrogen.

***** THE END *****

Institute of Applied Geophysics
of the
USSR Academy of Sciences

Entered on 24 February 1961

Translated by ANDRE L. BRICHANT
for the
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

APR 9 1962

References follow..

REFERENCES

1. D. R. BATES. Ann. Geophys., 8, 194, 1952.
2. M. NICOLET. Ann. Geophys., 15 (1), 1, 1959.
3. V. G. ISTOMIN. ISZ (AES), vyp. 4, 171, 1960.
4. V. G. ISTOMIN., ISZ (AES), vyp. 7, 1961.
5. V. G. ISTOMIN. Dokl. A.N.SSSR, 129 (1), 81, 1959.
6. R. B. BRYAN, R. B. HOLT, O. OLDENBERG. Phys.Rev., 106, 83, 1957.
7. E. P. BIALECKE, A. A. GOUGOL., J. Geophys.Res, 63, 3, 539, 1958.
8. A. D. DANILOV., ISZ(AES), v. 5, 60, 1960.
9. A. D. DANILOV., ISZ(AES), v. 8, 1961.
10. K. I. GRINGAUZ., Dokl. A.N.SSSR, 120 (6), 1234, 1958.
11. M. NICOLET. The Earth as a Planet, p. 644, 1953.
12. S. K. MITRA. Verkhnyaya atmosfera (Upper Atmosphere), IL, 1955.
13. A. S. JURSA, Y. TANAKA, LE BLANS, Pl. Sp. Sci. 1, 3, 1959.
14. T. VIOLETT, W. RENSE. J. Geophys. Res. 130 (3), 954, 1959.
15. G. S. IVANOV-KHOLODNYY, G. M. NIKOL'SKIY, Astron.Zh, 38, 45, 1961.
16. V. V. KATYUSHINA. Izv. A.N.SSSR, 10, 1960 (ser.geofizicheskaya)
17. A. D. DANILOV. Geomagnetizm i Aeronomiya, T.I, No.1, 45, 1961.
18. D. R. BATES. Proc. Roy. Sci., A253, No. 1275,452, 1959.